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(54) Title: TEST METHOD FOR EVALUATING SOLUBLE POLYMER GROWTH WHEN RECYCLING INHIBITOR
STREAMS

(57) Abstract: An improvement in a method for evaluating the efficiency of polymerization inhibitors is disclosed, wherein the improvement comprises: A) producing dissolved polymer in a solution comprising monomer and at least one inhibitor by means of any test known in the art to be useful for evaluating polymerization inhibitors, B) collecting the polymer-containing solution, C) measuring the degree of polymerization of the monomer in the collected solution, and D) re-subjecting the polymer-containing solution to the test conditions of A).

TEST METHOD FOR EVALUATING SOLUBLE POLYMER GROWTH WHEN RECYCLING INHIBITOR STREAMS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to a test method for evaluating the effectiveness of various compounds in their ability to prevent polymer growth via a "living" polymerization mechanism when the "living" polymer is dissolved in the monomer stream.

2. Description of Related Art

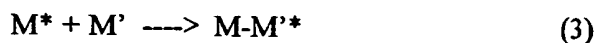
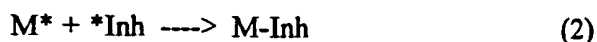
Many ethylenically unsaturated monomers undesirably polymerize at various stages of their manufacture, processing, handling, storage, and use. Polymerization, such as thermal polymerization, during their purification results in the loss of the monomer, i.e., a lower yield, and an increase in the viscosity of any tars that may be produced. The processing and handling of the higher viscosity tars then requires higher temperature and work (energy cost) to remove residual monomer.

A wide variety of compounds has been proposed and used for inhibiting uncontrolled and undesired polymerization of ethylenically unsaturated monomers. However, many of these compounds have not been fully satisfactory. Accordingly, there has been a continuing need in the art for a testing means by which compositions intended for use as monomer polymerization inhibitors can be evaluated.

There are several mechanisms by which polymerization inhibitors work. One mode of action for polymerization inhibitors is for the inhibiting species to combine with the propagating polymer chain such that the polymerization of that polymer chain stops, i.e., a termination reaction. If such an inhibitor-terminated polymer chain is capable of participating in a dynamic

equilibrium between a dormant species (the inhibitor-terminated chain) and an active polymer chain, it would be considered a "living" or quasiliving polymer. For example, Ivan, *Macromol. Symp.* 88:201-215 (1994) describes quasiliving polymerization as a polymerization in which "... only a portion of chain ends are active (propagating) and these are in equilibria with inactive (dormant, nonpropagating) chains..." Shigemoto *et al.*, *Macromol. Rapid Commun.* 17:347-351 (1996) state, "Well-defined polymers can be prepared by controlled / "living" radical polymerization in the presence of relatively stable radicals. These systems employ the principle of dynamic equilibration between dormant species and growing radicals via reversible homolytic cleavage of a covalent bond in dormant species." Further, Greszta *et al.*, *Macromolecules* 29:7661-7670 (1996) state, "The reversible homolytic cleavage of dormant species can be accomplished by either thermal, photochemical, or catalytic activation. The most successful approaches are as follows: homolytic cleavage of alkoxyamines and dithiocarbamates, use of various organometallic species, and catalyzed atom transfer radical polymerization." Such a "living" polymer is capable of increasing in molecular weight (growing) through its reaction with additional monomer units of the same or different types of polymerizable monomers.

The method by which this "living" polymer grows is termed the "living" polymerization mechanism, and is depicted below.



5 Reactions (1) and (2) depict the dynamic equilibrium, with (2) being the termination reaction. Reaction (3) depicts growth of the polymer chain. Reaction (4) depicts re-termination of the growing polymer chain with the inhibiting species. The amount of growth over any period of time is dependent on the relative rate at which (2) occurs versus (3), as long as (1) occurs to some extent. The faster (2) is relative to (3), the more time is needed for significant growth of the polymer. Under the conditions in which inhibitors are normally used, the concentration of the inhibiting species should be sufficiently high to cause reaction (2) to be much faster than reaction (3), otherwise it would not be an effective inhibiting system for commercial use. However, we have realized that even at an effective inhibiting amount of the inhibitor, growth can still occur, given sufficient time and temperature.

15 There are at least two scenarios in which "living" polymer can remain in a monomer purification train for an excessive amount of time.

First, the use of recycle can significantly increase the amount of time that the "living" polymer can remain in the purification train. To recycle unused inhibitor that is left in the purification stream after removal of the monomer, a portion of the residual stream is added to a feed stream earlier in the purification train. This residual stream typically contains inhibitor, small amounts of monomer, impurities in the monomer stream that have been concentrated by the purification process, and polymer formed during the purification process. Recycling this polymer will allow it time to grow if it is "living" polymer and the conditions of the

purification train allow the "living" polymerization mechanism to occur. If this polymer grows via the "living" polymerization mechanism, excessive polymerization would cause loss in product yield, increased waste residues from the process, and potential plugging of equipment due to excessively high molecular weight polymer in the purification stream.

5 Second, occasionally, conditions in the plant/purification process can result in the formation of polymer within the purification train that is not dissolved by the monomer stream. If this polymer is caught in a deadspace, or if it attaches to the metal on the inside of the equipment, it will not be washed out of the system. Thus, the polymer will remain within the system indefinitely (potentially for two or more years). If this polymer grows via the "living"

10 polymerization mechanism, it could coat the inside of the equipment, causing inefficient separation of the monomer stream components and/or insufficient heating of the stream to enable purification. Such a situation would cause loss in product yield and could potentially cause an unscheduled shut-down of the plant in order to clean out the undissolved polymer in the equipment. Such a shut-down results in loss of monomer production and additional

15 expense to clean out and dispose of the undissolved polymer.

SUMMARY OF THE INVENTION

Given the potential loss in monomer yield as well as loss in monomer production and the additional economic drawbacks due to increased waste residues and cleaning of plugged

20 equipment, a test method has now been developed to evaluate the effectiveness of various compounds in their ability to prevent polymer growth via a "living" polymerization mechanism when the "living" polymer is dissolved in the monomer stream.

This test method comprises:

A) producing polymer in solution via any test normally used to evaluate polymerization inhibitors, such as, but not limited to, static tests, dynamic tests, small scale simulations of a distillation column and/or reboiler, and pilot units for a distillation train,

B) collecting the polymer-containing solution, and

5 C) re-subjecting the polymer-containing solution to the test conditions.

More particularly, the present invention is directed to an improvement in a method for evaluating the efficiency of polymerization inhibitors, wherein the improvement comprises:

A) producing dissolved polymer in a solution comprising monomer and at least one inhibitor by means of any test known in the art to be useful for evaluating polymerization inhibitors,

10 B) collecting the polymer-containing solution,

C) measuring the degree of polymerization of the monomer in the collected solution, and

D) re-subjecting the polymer-containing solution to the test conditions of A).

15

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As stated above, the present invention is directed to a test method that comprises:

A) producing polymer in solution via any test normally used to evaluate polymerization inhibitors, such as, but not limited to, static tests, dynamic tests, small scale simulations of a distillation column and/or reboiler, and pilot units for a distillation train,

20

B) collecting the polymer-containing solution, and

C) re-subjecting the polymer-containing solution to the test conditions.

Typically, fresh inhibitor is added to the polymer-containing solution in an amount that

would bring the total level of inhibitor to the level charged in the initial test. The process of collecting polymer-containing solution and re-subjecting it to the reaction conditions (with additional inhibitor added) can be, and usually is, repeated several times. This is termed a "Multi-Pass Test" with each subjection to the test conditions constituting a single "pass."

5 The effects of each pass can be measured in many ways, including, but not limited to, measurement of the amount of polymer made during the pass, measurement of the concentration of polymer at steady-state (for dynamic tests), measurement of the induction time to polymerization (for static tests), and measurement of the molecular weight (M_w , M_n , M_z) and molecular weight distribution (MWD, M_w/M_n) of polymer made during the pass.

10 The advantages and the important features of the present invention will be more apparent from the following examples.

EXAMPLES

Procedure for Multi-Pass Reboiler Test

15 **Preparation of First Pass Feed Solution:**

Tert-butylcatechol (TBC) is removed from commercially available styrene by distillation under vacuum. Removal of TBC is verified by caustic titration. The desired amount of inhibitor(s) is added to this TBC-free styrene either directly or by first making a concentrated solution of the inhibitor in TBC-free styrene followed by further dilution with TBC-free styrene.

20 **Preparation of Second and Third Pass Feed Solutions:**

The Bottoms Stream from the previous Pass is collected except for the material in the Pot at the end of the run. The amounts of inhibitor(s) in the First Pass Feed Solution and the Bottoms

Stream from the First Pass are determined by appropriate analytical method(s), e.g., gas chromatography. An amount of inhibitor(s) is added to the collective Bottoms Stream from the First Pass to increase the level of inhibitor(s) in the Bottoms Stream to a level equal to that found in the First Pass Feed Solution. An equivalent amount of inhibitor(s) is added to the collective Bottoms Streams for subsequent Passes.

Procedure for Reboiler Test (a dynamic test):

A quantity of the Feed Solution containing inhibitor (blend) at the desired charge (stated as a wt/wt total inhibitor to styrene) is added to a round-bottom flask (the Pot) and heated to the desired temperature (usually 130° C.) and brought to reflux by adjusting the pressure/vacuum.

Once the Pot contents are at temperature, a continuous stream of fresh Feed Solution is begun at a rate that will add the volume of the initial Pot solution to the Pot over a period of time called the residence time (typically, one hour). At the same time that the fresh Feed Solution flow is begun, the Bottoms Stream flow is also begun. The Bottoms Stream is solution in the Pot that is removed at the same rate as the fresh Feed Solution is added. The equal flows of Feed and Bottoms Streams cause the quantity in the Pot to remain constant over the time of the experiment, while allowing continuous replenishment of inhibitor. This procedure simulates the way inhibitors are used in a distillation train of a plant producing vinyl monomers. The experiment continues with flow in and out of the Pot for a specified period of time. Typically, the First Pass runs for 10 hours, the Second Pass runs for 9 hours, the Third Pass runs for 8 hours, etc.

Samples are collected hourly from the Bottoms Stream. These samples are analyzed for polymer content via the methanol turbidity method. The amount of polymer in the samples is an indication of effectiveness of the inhibitor system being tested. "Average Polymer Make" is the

average of the polymer content values for samples taken after 4 hours running. The difference in the amount of polymer made in one Pass versus subsequent Passes is an indication of the ability of the inhibiting system to prevent or allow polymer to grow. For example, an increase in the amount of polymer made going from one Pass to the next which is roughly equivalent to the amount of polymer made during the First Pass is an indication that polymer is not growing under the test conditions. Conversely, an increase in the amount of polymer made going from one Pass to the next which is dramatically greater (about 10 times or more) than the amount of polymer made during the First Pass is an indication that polymer is growing under the test conditions.

The material left in the Pot at the end of the run is quickly removed and cooled, to stop any further polymerization. The material is then concentrated, if necessary, under reduced pressure at 40° C. until the polymer content is > 5 wt %. A sample of this polymer solution is then analyzed by Gel Permeation Chromatography (GPC) to determine the weighted average molecular weight (M_w) of the polymer. The difference in the M_w of the polymer made in one Pass versus subsequent Passes is an indication of the ability of the inhibiting system to prevent or allow polymer to grow. Any significant increase in M_w of the polymer made in one Pass versus the previous Pass is an indication that the polymer is growing under the test conditions.

This test is illustrated by the following examples in TABLE 1.

TABLE 1		
Inhibitor System / Pass	Average Polymer Make (wt%)	M _w of Polymer
300 ppm 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (4-oxo-TEMPO)		
Pass 1	0.052	3,910
Pass 2 (+ 150 ppm 4-oxo-TEMPO)	1.45	17,000
Pass 3 (+ 150 ppm 4-oxo-TEMPO)	7.45	31,700
900 ppm PDA; 600 ppm DNBP; 7 cc/min air		
Pass 1	0.066	5,160
Pass 2 (+ 65 ppm PDA/270 ppm DNBP)	0.183	5,150
Pass 3 (+ 65 ppm PDA/270 ppm DNBP)	0.423	5,740
1500 ppm DNBP		
Pass 1	0.109	3,990
Pass 2 (+ 435 ppm DNBP)	0.266	4,170
Pass 3 (+ 435 ppm DNBP)	0.430	4,500

PDA = N-phenyl-N'-(1,4-dimethylpentyl)-para-phenylenediamine

DNBP = 2,4-dinitro-6-sec-butylphenol

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.

CLAIMS

What is claimed is:

1. In a method for evaluating the efficiency of polymerization inhibitors, the improvement
5 comprising:

A) producing dissolved polymer in a solution comprising monomer and at least one inhibitor by means of any test known in the art to be useful for evaluating polymerization inhibitors,

B) collecting the polymer-containing solution,

10 C) measuring the degree of polymerization of the monomer in the collected solution, and

D) re-subjecting the polymer-containing solution to the test conditions of A).

2. The method of claim 1 further comprising the step of adding fresh inhibitor to the
15 solution prior to re-subjecting the polymer-containing solution to the test conditions of A).

3. The method of claim 2 wherein the fresh inhibitor is added to the polymer-containing solution in an amount sufficient to bring the total level of inhibitor to the level charged in the initial test.

20 4. The method of claim 1 wherein the test of step A) is selected from the group consisting of static tests, dynamic tests, small scale simulations of a distillation column and/or reboiler, and pilot units for a distillation train.

5. The method of claim 1 wherein the measurement step employs a technique selected from the group consisting of measurement of the amount of polymer made during a pass, measurement of the concentration of polymer at steady-state, measurement of the induction time to polymerization, and measurement of the molecular weight and molecular weight
- 5 distribution of polymer made during a pass.
6. The method of claim 1 wherein the monomer is styrene.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 G01N33/44 C08F2/00 C08F12/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 G01N C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 02400 A (A H MARKS AND COMPANY LIMITED ;CALLIN ROBERT CHARLES (GB); PRYCE A) 22 January 1998 (1998-01-22)	1,6
Y	page 8, line 12 - line 16 page 9, line 6 - line 17 page 10, line 12 - line 14	4,5
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *Z* document member of the same patent family		
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer Joyce, D

INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4 692 544 A (GOERNER RICHARD N ET AL) 8 September 1987 (1987-09-08) column 4, line 13 -column 5, line 52 -----	1
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INTERNATIONAL SEARCH REPORT

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